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(54) Title: POLYCARBONATE/POLYESTER BLENDS WITH IMPROVED THERMAL MELT STABILITY (57) Abstract <p>Impact modified polycarbonate/polyester blends have improved thermal melt stability when containing a low-ion polymeric impact modifier. The low-ion polymeric impact modifier contains 5-80 percent rubber by weight, and is characterized by having a thermal-melt-stabilizing ion content, which (i) in a polymeric impact modifier containing more than 1.0 up to 5.0 wt. percent anti-oxidant, (A) is an ion content of sodium and potassium ions of not more than 1,500 ppm, and (B) is an ion content of all ions of not more than 1,700 ppm; and (ii) in a polymeric impact modifier containing 0.1 to 1.0 wt. percent anti-oxidant, (A) is an ion content of sodium and potassium ions of not more than 800 ppm, and (B) is an ion content of all ions of not more than 1,500 ppm. Reducing the ion content of a polymeric impact modifier in a polycarbonate composition reduces the degradative effect of ionic species on the composition at high temperature.</p>		

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POLYCARBONATE/POLYESTER BLENDS WITH
IMPROVED THERMAL MELT STABILITY

5 This invention involves a composition of matter
having improved thermal melt stability, formed from an
admixture of polycarbonate and a polymeric impact
modifier, or polycarbonate, polyester and a polymeric
10 impact modifier. This invention also involves a method
of improving the thermal melt stability of a composition
formed from polycarbonate and a polymeric impact
modifier, or from polycarbonate, polyester and a
polymeric impact modifier.

15 Polycarbonate has found many uses because it
combines, in general, a high level of heat resistance
and dimensional stability with good insulating and non-
corrosive properties, and it is easily molded. However,
molding and other processing operations involving
polycarbonate frequently require temperatures at the
upper end of the range usually applicable to
20 thermoplastics. These higher temperatures are needed
because of the high melt strength of polycarbonate,
especially varieties which contain halogen or bulky
organic substituents on the polymer chain. Processing
25 of polycarbonate thus often occurs in the range of 230°C

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to 320°C. Moreover, molten material can remain at such elevated temperatures in a molding machine for extended periods of time, for example as long as thirty minutes, depending on the size of the object being molded, the size of the molding machine and the cycle time.

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At such elevated temperatures, the thermal melt stability of polycarbonate, as well as blends of polycarbonate with other substances such as polyester, becomes a concern. Lengthy exposure of polycarbonate or polycarbonate alloys to high temperatures can result in polymer degradation and/or transesterification. This appears to be a particular problem when polycarbonate and polyester are blended with a polymeric impact

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modifier. It would consequently be desirable to provide impact modified polycarbonate compositions which have improved thermal melt stability, and to provide methods for improving the thermal processing stability of such polycarbonate compositions.

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In one aspect, therefore, this invention involves a composition of matter comprising, in admixture, an aromatic polycarbonate, and a polymeric impact modifier which (a) contains 5-80 wt percent rubber, (b) contains more than 1.0 wt percent up to 5.0 wt percent anti-oxidant, and (c) has a content of sodium ions and potassium ions of not more than 1,500 weight parts per million ("ppm").

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In another aspect, this invention involves a composition of matter comprising, in admixture, an aromatic polycarbonate, and a polymeric impact modifier which (a) contains 5-80 wt percent rubber, (b) contains 0.1 to 1.0 wt percent anti-oxidant, and (c) has a

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content of sodium ions and potassium ions of not more than 800 weight ppm.

5 In yet another aspect, this invention involves a composition of matter comprising, in admixture, an aromatic polycarbonate, an aromatic polyester and a polymeric impact modifier containing 5-80 wt percent rubber, said composition being characterized in that it experiences no more than 2.0 percent weight loss after heating at 310°C in a thermogravimetric analyzer for ten minutes, no more than 3.5 percent weight loss after such heating for twenty minutes, and no more than 5.0 percent weight loss after such heating for thirty minutes.

15 In a further aspect, this invention involves a method of improving the thermal melt stability of an aromatic polycarbonate composition, comprising (a) providing (i) a polymeric impact modifier which contains more than 1.0 wt percent up to 5.0 wt percent anti-oxidant, and has a content of sodium ions and potassium ions of not more than 1,500 weight parts per million; or (ii) a polymeric impact modifier which contains 0.1 to 1.0 wt percent anti-oxidant, and has a content of sodium ions and potassium ions of not more than 800 weight parts per million; and (b) blending one or both of said polymeric impact modifiers with an aromatic polycarbonate.

30 When a polymeric impact modifier is admixed with a polycarbonate or with a composition containing polycarbonate and polyester, if the polymeric impact modifier contains reduced levels of ionic species or has a low ion content, the thermal melt stability of the polycarbonate composition is increased over that which

the composition displays if the polymeric impact modifier is not of the variety which has a low ionic species content. It has been found that ionic species in a polycarbonate composition can cause chain scission, polymer degradation and/or transesterification at high temperatures in the melt because the heat-activated ions promote polymer chain cleavage and/or decomposition. Reducing the ion content in a polycarbonate composition by using a low-ion polymeric impact modifier therefore increases the thermal melt stability of the composition because the extent of the decomposition-promoting effect of fewer ions is less harmful to the components of the composition.

The polycarbonate compositions of this invention are useful, for example, in the production of films, fibers, extruded sheets, multi-layer laminates and molded or shaped articles of virtually all varieties, especially appliance and instrument housings and components for use in the automotive and electronics industries. The methods of this invention are useful for making polycarbonate compositions to be employed in applications such as the foregoing.

The compositions of this invention are those in which (a) an aromatic polycarbonate, or a blend of (a) an aromatic polycarbonate and (b) an aromatic polyester, has been admixed with (c) a low-ion polymeric impact modifier containing 5-80 percent rubber by weight. The low-ion polymeric impact modifier used herein is characterized as having a thermal-melt-stabilizing ion content, which (i) in a polymeric impact modifier containing more than 1.0 up to 5.0 wt percent anti-oxidant, (A) is an ion content of sodium and potassium

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ions of not more than 1,500 ppm and preferably not more than 1,000 ppm, and (B) is an ion content of all ions of not more than 1,700 ppm; and (ii) in a polymeric impact modifier containing 0.1 to 1.0 wt percent anti-oxidant, (A) is an ion content of sodium and potassium ions of not more than 800 ppm and preferably not more than 650 ppm, and (B) is an ion content of all ions of not more than 1,500 ppm.

As a result of containing a low-ion polymeric impact modifier, the compositions of this invention are themselves characterized as having an ion content of not more than 1,200 ppm of either cations or anions, and are thereby further characterized as having increased thermal melt stability as compared to those compositions containing an impact modifier which is not of the low-ion variety. The level of ion content in an impact-modified polycarbonate composition is affected not only by the amount of polymeric impact modifier present in the composition in relation to polycarbonate and polyester, but also by sources of ions other than the polymeric impact modifier.

The compositions of this invention are further characterized in that they experience (i) no more than 2.0 percent weight loss, and preferably no more than 1.5 percent weight loss, after being heated at a temperature in excess of 300°C, for example 300°C-330°C for ten minutes; (ii) no more than 3.5 percent weight loss, and preferably no more than 3.0 percent weight loss, after such heating for twenty minutes; and (iii) no more than 5.0 percent weight loss, and preferably no more than 4.5 percent weight loss, after such heating for thirty minutes.

Suitable ranges of content for components (a), (b) and (c) in the compositions of this invention, expressed in parts by weight, are as follows:

- 5 (a) aromatic polycarbonate from 5 parts to 95 parts, and preferably from 10 parts to 85 parts,
- 10 (b) aromatic polyester up to 95 parts, and preferably from 10 parts to 70 parts, and
- 15 (c) polymeric impact modifier from 1 part to 40 parts, and preferably from 3 parts to 20 parts.

Preparation of the compositions of this invention can be accomplished by any suitable mixing means known in the art. Typically the substance(s) to be admixed with polycarbonate are dry blended in particulate form with sufficient agitation to obtain thorough distribution thereof within the polycarbonate. If desired, the dry-blended formulation can further, but need not, be melt mixed in an extruder. Mixing rolls, a dough-mixer or a Banbury mixer can also be used in the blending process. Alternatively, a master batch formulation can be prepared containing polycarbonate or polyester and the substance(s) to be admixed or blended with it wherein polycarbonate or polyester is present in only a minor proportion, *e.g.* 20 percent. The master batch is then available for storage or shipment, and can be diluted with additional polycarbonate or polyester at the time of use. The compositions of this invention can be formed or molded using conventional techniques such as compression, injection, calendering, vacuum forming,

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extrusion and/or blow molding techniques, alone or in combination. The compositions can also be formed into films, fibers, multi-layer laminates or extruded sheets on any machine suitable for such purpose.

5 (a) Polycarbonate. The aromatic polycarbonates suitable for use in the present invention are produced by any of the conventional processes known in the art for the manufacture of polycarbonates. Generally,
10 aromatic polycarbonates are prepared by reacting an aromatic dihydric phenol with a carbonate precursor, such as phosgene, a haloformate or a carbonate ester.

A preferred method for preparing suitable
15 polycarbonates involves the use of a carbonyl halide, such as phosgene, as the carbonate precursor. This method involves passing phosgene gas into a reaction mixture containing an activated dihydric phenol, or a nonactivated dihydric phenol and an acid acceptor, such
20 as pyridine, dimethyl aniline, quinoline and the like. The acid acceptor may be used undiluted or diluted with inert organic solvents, such as methylene chloride, chlorobenzene or 1,2-dichloroethane. Tertiary amines are advantageous since they are good solvents as well as
25 acid acceptors during the reaction.

The temperature at which the carbonyl halide reaction proceeds may vary from below 0°C to 100°C. The reaction proceeds satisfactorily at temperatures from
30 room temperature to 50°C. Since the reaction is exothermic, the rate of phosgene addition may be used to control the temperature of the reaction. The amount of phosgene required will generally depend upon the amount of dihydric phenol present. Generally speaking, one mole of phosgene will react with one mole of dihydric

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phenol to form the polycarbonate and two moles of HCl. The HCl is in turn taken up by the acid acceptor.

Another method for preparing the aromatic polycarbonates useful in this invention involves adding
5 phosgene to an alkaline aqueous suspension of dihydric phenols. This is preferably done in the presence of inert solvents such as methylene chloride, 1,2-dichloroethane and the like. Quaternary ammonium compounds may be employed to catalyze the reaction.

Yet another method for preparing such aromatic polycarbonates involves the phosgenation of an agitated suspension of an anhydrous alkali salt of an aryl diol
15 in a nonaqueous medium such as benzene, chlorobenzene or toluene. The reaction is illustrated by the addition of phosgene to a slurry of the sodium salt of, for example, Bisphenol A in an inert polymer solvent such as chlorobenzene.

20 Generally speaking, a haloformate such as the bis-haloformate of Bisphenol A may be used in place of phosgene as the carbonate precursor in any of the methods described above.

25 When a carbonate ester is used as the carbonate precursor in the polycarbonate-forming reaction, the materials are reacted at temperatures in excess of 100°C for times varying from 1 to 15 hours. Under such
30 conditions, ester interchange occurs between the carbonate ester and the dihydric phenol used. The ester interchange is advantageously consummated at reduced pressures on the order of from 10 to 100 millimeters of mercury, preferably in an inert atmosphere such as nitrogen or argon.

Although the polymer-forming reaction may be conducted in the absence of a catalyst, one may, if desired, employ a typical ester exchange catalyst, such as metallic lithium, potassium, calcium or magnesium. The amount of such catalyst, if used, is usually small, ranging from 0.001 percent to 0.1 percent, based on the weight of the dihydric phenols employed.

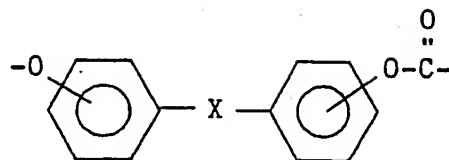
In the solution methods of preparation, the aromatic polycarbonate emerges from the reaction in either a true or pseudo solution depending on whether an aqueous base or pyridine is used as an acid acceptor. The copolymer may be precipitated from the solution by adding a polymer nonsolvent, such as heptane or isopropanol. Alternatively, the polymer solution may be heated, typically under reduced pressure, to evaporate the solvent.

The methods and reactants described above for preparing carbonate polymers suitable for use in the practice of this invention are discussed in greater detail in Schnell, US Pat. No. 3,028,365; Campbell, US Pat. No. 4,384,108; Glass, US Pat. No. 4,529,791; and Grigo, US Pat. No. 4,677,162.

A preferred aromatic polycarbonate is characterized by repeated units corresponding to the general formula:

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wherein X is a divalent C_1-C_{15} hydrocarbon radical, a single bond, -O-, -S-, -S₂-, -SO-, -SO₂-, or -CO-. Each aromatic ring may additionally contain, instead of hydrogen, up to four substituents such as C_1-C_4 alkyl hydrocarbon or alkoxy radicals, aryl or aryloxy radicals, or halo radicals.

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Although the polycarbonates mentioned above, such as those derived from 2,2-bis(4-hydroxyphenyl)propane ("Bisphenol-A" or "Bis-A") or from 1,1-bis(4-hydroxyphenyl)-1-phenyl ethane ("Bisphenol-A-P" or "Bis-A-P"), can each be employed in this invention as a homopolymer, the carbonate polymers used herein can also be derived from two or more bisphenols, or two or more acid- or hydroxy-terminated reactants such as dicarboxylic acids or alkylene glycols, or from two or more different dihydroxy compounds, or mixtures of any of the foregoing, in the event a carbonate copolymer or interpolymer, such as a copolyester/carbonate is desired, rather than a homopolymer.

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Copolymers can be formed, for example, when a bisphenol is reacted with a carbonic acid derivative and a polydiorganosiloxane containing α,ω -bishydroxyaryloxy terminal groups to yield a siloxane/carbonate block copolymer [as are discussed in greater detail in Paul, USP 4,569,970], or when a bisphenol is reacted with a

bis(ar-haloformylaryl) carbonate to yield an alternating copolyestercarbonate. The bis(ar-haloformylaryl) carbonate is formed by reacting a hydroxycarboxylic acid with a carbonic acid derivative under carbonate forming conditions, and the copolyestercarbonates are discussed in greater detail in Swart, USP 4,105,533.

The term "polycarbonate" as used herein, and in the claims appended hereto, should therefore be understood to include carbonate homopolymers, carbonate copolymers (as described above), and/or blends of carbonate homopolymers and/or carbonate copolymers.

(b) Polyester. The aromatic polyester used in this invention may be made by a variety of methods. Although the self-esterification of hydroxycarboxylic acids is known, direct esterification, which involves the reaction of a diol with a dicarboxylic acid with the resulting elimination of water, is a more frequently used method for commercial production, giving an -[AABB]- polyester. Although the presence of a catalyst such as p-toluene sulfonic acid, a titanium alkoxide or a dialkyltin oxide is helpful, the primary driving force behind the direct esterification reaction is heat. Temperatures applied exceed the melting points of the reactants and typically approach the boiling point of the diol being used, and usually range from 150°C to 280°C. An excess of the diol is typically used, and once all of the acid has reacted with diol, the excess diol is removed by distillation with the application of additional heat under reduced pressure. The ester of the diacid initially formed from the diol, having -OH end groups, undergoes alcoholysis and polymerization to form polymeric esters and the diol is split out as a byproduct and removed from the reaction.

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zone. The reaction is typically carried out in the presence of an inert gas.

Alternatively, but in like manner, ester-
5 forming derivatives of a dicarboxylic acid can be heated with a diol to obtain polyesters in an ester interchange reaction. Suitable acid derivatives for such purpose are esters, halides, salts or anhydrides of the acid. When a bis ester of the diacid is used for purposes of
10 the interchange reaction, the alcohol from which the ester is formed (the alcohol to be displaced) should be lower boiling than the diol to be used for formation of polyester (the displacing alcohol). The reaction can
15 then be conveniently run at a temperature at or below the boiling point of the displacing alcohol but well above that of the displaced alcohol, and is usually run in a temperature range similar to that for direct esterification. The ester interchange reaction is
20 typically run in the presence of a diluent, for example, an inert organic solvent such as chloroform or tetrachloroethane, and in the presence of a base, for example a tertiary organic base such as pyridine. Typical catalysts used when ester interchange involves
25 alcoholysis are weak bases such as carbonates or alkoxides of sodium, lithium, zinc, calcium, magnesium or aluminum, whereas catalysts such as antimony oxide, titanium butoxide or sodium acetate are often used when
30 acidolysis occurs in the interchange reaction. Diol derivatives such as an acetate can be used effectively when it is desired to conduct acidolysis.

Maintenance of high temperature is an important aspect of esterification, particularly toward the end of the reaction. As a consequence, thermal ester scission

competes with polymer growth as the prevailing result of the process, which places an upper limit on the molecular weight which can be achieved through the use of melt polymerization. The molecular weight of polyester can be increased by adding a chain coupling agent, such as diphenyl carbonate, to the melt reaction mixture just prior its completion. Or, to achieve higher weight by solid state polymerization, polyester product of intermediate weight can be heated in a vacuum or stream of inert gas, first to a temperature where it crystallizes and then to a temperature close to its melting point.

Polyesters can also be produced by a ring-opening reaction of cyclic esters or lactones, for which organic tertiary bases and alkali and alkaline earth metals, hydrides and alkoxides can be used as initiators. Advantages offered by this type of reaction are that it can be run at lower temperatures, frequently under 100°C, and there is no need to remove a condensation product from the reaction.

Suitable reactants for making the polyester used in this invention, in addition to hydroxycarboxylic acids, are diols and dicarboxylic acids either or both of which can be aliphatic or aromatic. A polyester which is a poly(alkylene alkanedicarboxylate), a poly(alkylene phenylenedicarboxylate), a poly(phenylene alkanedicarboxylate), or a poly(phenylene phenylenedicarboxylate) is therefore appropriate for use herein. Alkyl portions of the polymer chain can be substituted with, for example, halogens, alkoxy groups or alkyl side chains and can contain divalent heteroatomic groups (such as -O-, -S- or -SO₂-) in the paraffinic segment of the chain. The chain can also

contain unsaturation and non-aromatic rings. Aromatic rings can contain substituents such as halogens, alkoxy or alkyl groups, and can be joined to the polymer backbone in any ring position and directly to the alcohol or acid functionality or to intervening atoms.

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Typical alkylene diols used in ester formation are the C₂ - C₁₀ glycols, such as ethylene-, propylene-, and butylene glycol. Alkanedicarboxylic acids frequently used are oxalic acid, adipic acid and sebacic acid. Diols which contain rings can be, for example, a 1,4-cyclohexylenyl glycol or a 1,4-cyclohexane-dimethylene glycol, resorcinol, hydroquinone, 4,4'-thiodiphenol, bis-(4-hydroxyphenyl)sulfone, a dihydroxynaphthalene, a xylylene diol, or can be one of the many bisphenols such as 2,2-bis-(4-hydroxyphenyl)propane. Aromatic diacids include, for example, terephthalic acid, isophthalic acid, naphthalenedicarboxylic acid, diphenyletherdicarboxylic acid, diphenyldicarboxylic acid, diphenylsulfonedicarboxylic acid, diphenoxyethanedicarboxylic acid.

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In addition to polyesters formed from one diol and one diacid only, the term "polyester" as used herein includes random, patterned or block copolyesters, for example those formed from two or more different diols and/or two or more different diacids, and/or from other divalent heteroatomic groups. Mixtures of such copolyesters, mixtures of polyesters derived from one diol and diacid only, and mixtures of members from both of such groups, are also all suitable for use in this invention, and are all included in the term "polyester". For example, use of cyclohexanedimethylol together with ethylene glycol in esterification with terephthalic acid

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forms a clear, amorphous copolyester ("PETG") of particular interest. Also contemplated are PCTG; liquid crystalline polyesters derived from mixtures of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and ethylene glycol; or mixtures of terephthalic acid, 4-hydroxybenzoic acid and 4,4'-dihydroxybiphenyl.

Aromatic polyesters such as the poly(alkylene phenylenedicarboxylates) polyethylene terephthalate and polybutylene terephthalate, or mixtures thereof, are particularly useful in this invention.

Methods and materials useful for the production of polyesters, as described above, are discussed in greater detail in Whinfield, US Pat. No. 2,465,319, Pengilly, US Pat. No. 3,047,539 and Russell, US Pat. No. 3,756,986.

(c) Polymeric Impact Modifier. The polymeric impact modifiers useful in this invention are those which contain between five and eighty percent (5-80 percent) rubber by weight, and have a glass transition temperature (T_g) less than 0°C. T_g is the temperature or temperature range at which a polymeric material shows an abrupt change in its physical properties, including, for example, mechanical strength. T_g can be determined by differential scanning calorimetry.

(c)(i) Thermoplastic Elastomers. One group of polymeric impact modifiers suitable for use herein includes thermoplastic elastomers, many of which are based on an olefinic backbone. Representative examples of a few thermoplastic elastomers useful herein are the following:

Butyl rubber is an elastomer which is the product of copolymerizing isobutylene and isoprene where the isoprene typically makes up no more than 2.5 mole percent of the copolymer. Although the solution process is used to manufacture butyl rubber, most of it is made
5 by a precipitation (slurry) method wherein the monomers are copolymerized in methyl chloride diluent using a catalyst such as aluminum chloride. Butyl rubbers, as described above, are discussed in greater detail in
10 Green, USP 2,401,754 and Nelson, USP 2,462,123.

Although the presence of the pendant methyl group gives EPM (ethylene/propylene) rubber a structure similar to that of natural rubber, EPM rubber has no
15 double bonds in the backbone. The ratio of ethylene to propylene in EPM rubber is from 50/50 to 75/25. When a diene is copolymerized with ethylene and propylene, the product is known as EPDM rubber. EPM/EPDM rubbers can be copolymerized or grafted with vinyl monomers such as
20 styrene and acrylonitrile. EPM/EPDM rubbers, which can be made by the solution process, are described above and are discussed in greater detail in Paige, USP 3,341,503.

25 Formation of neoprene rubber by polymerization of 2-chloro-1,3-butadiene can result from addition involving both of the double bonds, or through just one of the two leaving the other as a pendant group. Neoprene rubber is typically made by free radical batch
30 emulsion polymerization, but can also be made in a continuous process. Neoprene rubber, as described above, is discussed in greater detail in Collins, USP 1,967,865 and Aho, USP 2,831,842.

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Nitrile rubber, which is polymerized from 1,3-butadiene and acrylonitrile, typically has 15-50 percent acrylonitrile content. It is usually preferred to make nitrile rubbers by emulsion. Nitrile rubber and methods for making same, as described above, are discussed in
5 greater detail in Konrad, USP 1,973,000.

As with rubbers involving derivatives of butadiene, formation of polybutadiene can be by either
10 1,4 or 1,2 (vinyl) addition of the butadiene molecule. Polybutadiene rubber is typically manufactured by solution polymerization, using organic lithium compounds or coordination catalysts containing metals in reduced valence states. Polybutadiene rubber, as described
15 above, is discussed in greater detail in Brockway, USP 2,977,349 and Ueda, USP 3,170,907.

Polyisoprene, with its pendant methyl group on what would otherwise be a butadiene unit, also
20 polymerizes in *cis*-1,4, *trans*-1,4 or 1,2 (vinyl) form. Ziegler catalysts can be used in the polymerization. Polyisoprene and methods for making same, as described above, are discussed in greater detail in Kahn, USP
25 3,165,503.

Polyether rubbers include epichlorohydrin elastomers, which can be prepared either by a coordination polymerization mechanism using an aluminum
30 alkyl-water catalyst in a hydrocarbon solvent, or in solution using benzene, toluene or methylene chloride as the solvent. Propylene oxide elastomers can also be prepared in solution, by copolymerization with allyl glycidyl ether, using a coordination catalyst such as diethyl zinc water. Polyether rubbers, as described

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above, are discussed in greater detail in Vandenberg, USP 3,634,303 and Vandenberg, USP 3,639,267.

5 An SBR rubber is a copolymer of styrene and butadiene which typically contains 23 percent styrene. The monomers themselves can be randomly dispersed along the backbone, or blocks of each monomer can be randomly dispersed. SBR rubbers, as described above, are discussed in greater detail in Zelinski, USP 2,975,160 and Zelinski, USP 3,281,383.

15 Polymeric impact modifiers can also include thermoplastic elastomers such as A-B-A or A-B block copolymers which have a rigid block "A" having a T_g above room temperature (approximately 23-25°C) and a rubbery block "B" having a T_g below room temperature. Examples of typical pairings of materials to form the respective A and B blocks of a block copolymer thermoplastic elastomer are shown in Table I.

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Table I
Block Copolymer Pairings

A block	B block
polystyrene	polybutadiene polyisoprene ethylene/butylene copolymer
polyethylene	ethylene/butylene copolymer
polyurethane	polyester polyether
polyester	polyether
polypropylene	EPDM rubber

Block copolymer thermoplastic elastomers can be prepared, for example, by anionic polymerization using an alkyl-lithium initiator. Hydrogenated styrene/ethylene-butylene/styrene block copolymers, such as that available from Shell Oil Co. as Kraton™ G-1651 rubber, are preferred.

Styrene-diene block copolymers, as described above, are discussed in greater detail in Holden, USP 3,265,766 and Prudene, USP 3,949,020. Thermoplastic elastomers based on urethane are discussed in greater detail in Schollenberger, USP 3,015,650 and Saunders, USP 3,214,411; and those based on copolyester-ether are discussed in Witsiepe, USP 3,651,014.

(c)(ii) Styrene/Acrylonitrile Copolymer. Also useful as a polymeric impact modifier herein is a styrene/acrylonitrile copolymer ("SAN") which is rubber-modified. An example of such a rubber-modified

styrene/acrylonitrile copolymer is an elastomeric-thermoplastic composite such as an acrylonitrile-butadiene-styrene copolymer ("ABS"). The elastomeric portion of such composite is usually dispersed as discrete particles in a matrix made up of the thermoplastic portion.

ABS is typically formed by the grafting of an SAN copolymer onto a polybutadiene substrate latex. The polybutadiene forms particles of rubber - the elastomeric component - which are dispersed as a discrete phase in a thermoplastic matrix formed by the SAN. This structural aspect of ABS - the dispersion of rubber particles in a compatible thermoplastic phase or matrix - is more important than the precise monomer content. The composite can be manufactured from nothing other than acrylonitrile, butadiene and styrene, or other monomers can be substituted or mixed in with them. Some of the monomers which are frequently substituted for or intermixed with acrylonitrile, butadiene and styrene are mentioned below in connection with the three usual methods of manufacturing ABS.

One method for making ABS resin is emulsion polymerization wherein the first step is the production of a rubber substrate latex in an aqueous emulsion. Soaps and surfactants are used in the emulsion process. The substrate results from polymerization, which can be initiated by organic peroxides, persulfates, iron, sugar, or peroxide redox systems, of 1,3-butadiene alone or in combination with other monomers. Butadiene can be copolymerized with either styrene or acrylonitrile to form the substrate, but numerous other comonomers yield equivalent results. In general, any mixture containing

a butadiene-1,3 hydrocarbon and a copolymerizable compound containing a single olefinic double bond, in proportions such that an unsaturated elastomeric copolymer - a rubber - is formed on polymerization of the mixture in aqueous emulsion, is appropriate. For example, there may be used mixtures containing a predominant amount of butadiene-1,3, isoprene, 2,3-dimethyl butadiene-1,3 or piperylene, or a combination of two or more of these and a lesser amount of one or more of the following monomers: styrene, alpha-methyl styrene, p-methoxy styrene, p-chloro styrene, dichloro styrene, vinyl naphthalene and other alkenyl substituted aromatic compounds of the formula



wherein Ar is an aromatic radical having its connecting valence on a ring carbon atom with R being as follows: hydrogen or alkyl; acrylonitrile, methacrylonitrile, ethacrylonitrile, alphachloro acrylonitrile, methyl methacrylate, ethyl methacrylate, isobutyl methacrylate, methyl acrylate, propyl acrylate, butyl acrylate, octyl acrylate, methyl alpha-chloro acrylate, methacrylamide, acrylamide, N.N-diethyl acrylamide and other nitriles, amides and alkyl esters of alpha-methylene aliphatic monocarboxylic acids; substituted aromatic maleimides such as N-phenyl maleimide; diethyl fumarate, diethylchloromaleate, vinylidene chloride, methyl vinyl ketone, methyl isopropenyl ketone, vinyl pyridines, vinyl furan, vinyl carbazole, isobutylene, ethylene, and the like. It is preferred that, in the preparation of the rubber latex, the proportion of butadiene to other monomers be in the range of 2/1 to 15/1.

After formation of the rubber latex substrate, the rubber latex substrate and styrene and acrylonitrile monomers are subjected to further aqueous emulsion wherein the rubber latex substrate makes up from 4
5 percent to less than 40 percent of the rubber-monomer mass charged to the reactor. The concentration of styrene is usually 1.5 to 3.5 times that of acrylonitrile. However other monomers such as
10 methacrylonitrile, divinylbenzene, α -methyl styrene, p-methyl styrene, methyl methacrylate, N-phenyl maleimide, chlorinated and brominated styrenes, and methyl-, ethyl- or n-butylacrylate, or mixtures thereof, may also be in conjunction with styrene and acrylonitrile. Organic
15 peroxides, azo compounds, persulfates, or redox systems are usually used to initiate polymerization. SAN is formed, some of which is grafted to the rubber latex substrate, and some of which is free. The latex containing both the grafted rubber and the free SAN is
20 then mixed with a coagulant solution, heated and agitated to produce discrete particles of ABS resin. The slurry containing those particles is dewatered in a centrifuge, and the resin is dried. Methods for making
25 ABS resin by emulsion polymerization, as described above, are discussed in greater detail in Childers, USP 2,820,773 and Calvert, USP 3,238,275, as well as in U.S. Patents 2,820,773, 3,162,695, 3,238,275, 3,864,428, 4,180,494, and 4,257,937.

30

When ABS is made by suspension polymerization, a pre-formed elastomeric component (i.e. a rubber), usually a polybutadiene or a butadiene/styrene copolymer, is dissolved in a mixture of styrene and acrylonitrile. The rubber component may be one of the

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several mentioned above with respect to emulsion polymerization of ABS, or may be polyisoprene, polycyclopentadiene, natural rubber, chlorinated rubber or copolymers of butadiene with isobutylene. However, the preferred rubber component is a linear 1,4 polybutadiene having a 35 percent to 50 percent cis content.

The preferred ratio of styrene to acrylonitrile in the styrene-acrylonitrile solution is 90/10 to 60/40, and in the preferred recipe the rubber component constitutes from 4 percent to less than 40 percent of the product. As with the emulsion process described above, numerous substances will function in a manner equivalent to that of styrene and may be substituted therefor, to-wit: alphas-methyl styrene, or other substituted vinyl aromatics such as vinyl-toluene, vinylxylene, vinyl-ethyl benzene or vinylchloro benzene. Methacrylonitrile is another alkenyl cyanide monomer which will serve in the place of acrylonitrile.

The rubber component, monomers and initiator are charged to the reaction vessel and polymerization ensues until a conversion rate of 15 percent to 30 percent is reached, resulting in the production of a prepolymer. Phase inversion occurs, and the rubber precipitates from solution and becomes the discontinuous phase dispersed as particles ranging from 0.5 to 5 μm in size. The prepolymer is then placed in a suspension reactor in an aqueous solution containing a suspending agent, initiator and chain transfer agent. Typical suspending agents are ionic surfactants and carboxymethyl cellulose, polyvinyl alcohol, methyl cellulose, sulfonated polystyrenes, polyglycol ethers

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and hydroxyethyl cellulose. Typical initiators for the polymerization which occurs during suspension are t-butyl perbenzoate, di-t-butyl peroxide, dibenzoyl peroxide, t-butyl peracetate or t-butylperoxy isopropyl carbonate. Agitation of the solution helps complete the polymerization. The process is completed by dewatering the slurry in a centrifuge, and moisture content is further reduced by flash drying. Manufacture of ABS by the suspension process, as described above, is discussed in greater detail in Carrock, USP 3,515,692 and Ackerman, USP 4,151,128.

In bulk or mass polymerization, ABS is formed by dissolving an elastomeric component (i.e. a rubber) in the monomer mix, which contains styrene, acrylonitrile, an initiator and, frequently, a chain transfer agent such as a mercaptan or a terpinolene. The reaction can, however, be thermally initiated. The styrene and acrylonitrile monomers polymerize, some grafting to the rubber component, but most forming a monomer-polymer solution. As the relative volume of the monomer-SAN polymer phase increases, discrete rubber particles become dispersed in the matrix resulting from the monomer-SAN polymer phase. The rubber particles are stabilized by being grafted to SAN polymers at the interface between the particles and the SAN polymer matrix. Additional stabilization is furnished when monomer becomes occluded, and polymerizes, within the rubber particles. Because polymerization occurs completely within a monomer/polymer medium, viscosity increases as conversion increases. To allow continued agitation of the reaction mixture despite such increasing viscosity, diluents such as methyl ethyl ketone and ethylbenzene are added to the reactor. Upon

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the completion of polymerization, the melt is devolatilized using equipment such as a devolatilizing extruder or a flash evaporator, and vacuum is applied to remove unreacted monomers and diluents.

5 As is true of ABS made by the emulsion or suspension method, numerous substances can be used in the bulk method in place of, or conjunction with, styrene, examples of such substances being as follows:

10 alpha-alkyl monovinylidene monoaromatic compounds, *e.g.* alpha-methylstyrene, alpha-ethylstyrene, alpha-methylvinyltoluene; ring-substituted alkyl styrenes, *e.g.* vinyl toluene, o-ethylstyrene, p-ethylstyrene, 2,4-dimethylstyrene; ring-substituted halostyrenes, *e.g.*, o-

15 chlorostyrene, p-chlorostyrene, o-bromostyrene, 2,4-dichlorostyrene; ring-alkyl, ring-halo-substituted styrenes, *e.g.* 2-chloro-4-methylstyrene and 2,6-dichloro-4-methylstyrene; methacrylates such as methyl

20 methacrylate; maleic acid and its esters and anhydrides; substituted aromatic maleimides such as N-phenyl maleimide; and mixtures of the foregoing. If so

25 desired, mixtures of such monovinylidene aromatic monomers may be employed. Methacrylonitrile can also be used in combination with acrylonitrile. Bulk methods for the preparation of ABS, as described above, are discussed in greater detail in Kruse, USP 4,187,260, Simon, USP 4,252,911 and Weber, USP 4,526,926.

30 What is set forth above concerning methods of making the rubber-modified styrene/acrylonitrile copolymer used in this invention from styrene, acrylonitrile and butadiene applies equally to the other forms of rubber-modified SAN which result from variation in the monomer mix. The rubber-modified

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styrene/acrylonitrile copolymer used in this invention can be made from any of the various monomers (or mixtures thereof), and can be made by any of the various methods, which are included above in the discussion relating specifically to the manufacture of ABS.

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Another form which the rubber-modified styrene/acrylonitrile copolymer can take is an AES (acrylonitrile/EPDM/styrene) copolymer, which is obtained when SAN is grafted to a substrate made up of an EPDM (ethylene/propylene/non-conjugated diene) rubber, as is discussed in greater detail in Henton, USP 4,766,175. SAN can also be crosslinked to an acrylate elastomer to form a rubber-modified SAN, as in the case of an ASA (acrylonitrile/styrene/acrylate) copolymer, which is discussed in greater detail in Yu, USP 3,944,631. Additionally, mixtures of the various copolymers described above can serve as the rubber-modified styrene/acrylonitrile copolymer of this invention. However, the preferred rubber-modified styrene/acrylonitrile copolymer is ABS.

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(c)(iii) Core-shell Graft Polymer. The core-shell graft polymers suitable for use in this invention as a polymeric impact modifier are characterized in that their structure comprises an elastomeric core based substantially on either a conjugated diene or an acrylate rubber, and a rigid grafted phase. These polymers are characterized in that the glass transition temperature of the elastomeric phase is below 0°C, and in that the elastomeric phase may optionally be at least partially crosslinked.

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A diene-based core-shell graft polymer contains a substrate latex, or core, which is made by polymerizing a diene, preferably a conjugated diene, or by copolymerizing a diene with a mono-olefin or polar vinyl compound, such as styrene, acrylonitrile, or an alkyl ester of an unsaturated carboxylic acid such as methyl methacrylate. The substrate latex is typically made up of 40-85 percent diene, preferably a conjugated diene, and 15-60 percent of the mono-olefin or polar vinyl compound. The elastomeric core phase should have a glass transition temperature ("T_g") of less than 10°C, and preferably less than -20°C. A mixture of monomers is then graft polymerized to the substrate latex. A variety of monomers may be used for this grafting purpose, of which the following are exemplary: vinyl compounds such as vinyl toluene or vinyl chloride; vinyl aromatics such as styrene, alpha-methyl styrene or halogenated styrene; acrylonitrile, methacrylonitrile or alpha-halogenated acrylonitrile; a C₁-C₈ alkyl acrylate such as ethyl acrylate or hexyl acrylate; a C₁-C₈ alkyl methacrylate such as methyl methacrylate or hexyl methacrylate; acrylic or methacrylic acid; and the like or a mixture of two or more thereof.

The grafting monomers may be added to the reaction mixture simultaneously or in sequence, and, when added in sequence, layers, shells or wart-like appendages can be built up around the substrate latex, or core. The monomers can be added in various ratios to each other although, when just two are used, they are frequently utilized in equal amounts. A typical weight ratio for methyl methacrylate/butadiene/styrene copolymer ("MBS" rubber) is 60-80 parts by weight

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substrate latex, 10-20 parts by weight of each of the first and second monomer shells. A preferred formulation for an MBS rubber is one having a core built up from 71 parts of butadiene, 3 parts of styrene, 4 parts of methyl methacrylate and 1 part of divinyl benzene; a second phase of 11 parts of styrene; and a shell phase of 11 parts of methyl methacrylate and 0.1 part of 1,3-butylene glycol dimethacrylate, where the parts are by weight of the total composition. A diene-based, core-shell graft copolymer elastomer and methods for making same, as described above, are discussed in greater detail in Saito, USP 3,287,443, Curfman, USP 3,657,391, and Fromuth, USP 4,180,494.

15 An acrylate-based core-shell graft polymer has a first phase forming an elastomeric core and a second phase forming a rigid thermoplastic phase said elastomeric core. The elastomeric core is formed by emulsion or suspension polymerization of monomers which consist of at least 50 weight percent alkyl and/or aralkyl acrylates having up to fifteen carbon atoms, and, although longer chains may be used, the alkyls are preferably C_2-C_6 , most preferably butyl acrylate. The elastomeric core phase should have a T_g of less than 10°C, and preferably less than -20°C.

30 The rigid thermoplastic phase of the acrylate rubber is formed on the surface of the elastomeric core using suspension or emulsion polymerization techniques. The monomers necessary to create this phase together with necessary initiators are added directly to the reaction mixture in which the elastomeric core is formed, and polymerization proceeds until the supply of monomers is substantially exhausted. Monomers such as

an alkyl ester of an unsaturated carboxylic acid, for example a C₁-C₈ alkyl acrylate like methyl acrylate, hydroxy ethyl acrylate or hexyl acrylate, or a C₁-C₈ alkyl methacrylate such as methyl methacrylate or hexyl methacrylate, or mixtures of any of the foregoing, are
5 some of the monomers which can be used for this purpose. Either thermal or redox initiator systems can be used. Because of the presence of the graft linking agents on the surface of the elastomeric core, a portion of the
10 chains which make up the rigid thermoplastic phase are chemically bonded to the elastomeric core. It is preferred that there be at least 20 percent bonding of the rigid thermoplastic phase to the elastomeric core.

15 A preferred acrylate rubber is made up of more than 40 percent to 95 percent by weight of an elastomeric core and 60 percent to 5 percent of a rigid thermoplastic phase. The elastomeric core can be polymerized from 75 percent to 99.8 percent by weight
20 C₁-C₈ acrylate, preferably n-butyl acrylate. The rigid thermoplastic phase can be polymerized from at least 50 percent by weight of C₁-C₈ alkyl methacrylate, preferably methyl methacrylate. Acrylate rubbers and
25 methods for making same, as described above, are discussed in greater detail in Owens, USP 3,808,180 and Witman, USP 4,299,928.

30 Mixtures of more than one of the various kinds of polymeric impact modifiers described above may be used herein as well.

The polymeric impact modifiers suitable for use in this invention are also characterized as having a thermal-melt-stabilizing ion content, but as having, in

any event, (i) in a polymeric impact modifier containing more than 1.0 up to 5.0 wt percent anti-oxidant, (A) an ion content of sodium and potassium ions of not more than 1,500 ppm and preferably not more than 1,000 ppm, and (B) an ion content of all ions of not more than 1,700 ppm; and (ii) in a polymeric impact modifier containing 0.1 to 1.0 wt percent anti-oxidant, (A) an ion content of sodium and potassium ions of not more than 800 ppm and preferably not more than 650 ppm, and (B) an ion content of all ions of not more than 1,500 ppm.

In the polymeric impact modifier, an anti-oxidant may be present in an amount from 0.1 wt percent to 1.0 wt percent, or in an amount from greater than 1.0 wt percent up to 5.0 wt percent. Representative anti-oxidants which are suitable for admixture with the polymeric impact modifier of this invention include phenolics such as hindered phenols, hydroquinones, bisphenols, and aryl and alkyl phosphites such as tri(mixed nonyl- and dinonylphenyl) phosphite, including substituted members of those groups and/or a mixture of more than one thereof. Among the foregoing are tris(2,4-di-tert-butylphenyl) phosphite; 1,6-hexamethylene bis-(3,5-di-tert-butyl-4-hydroxyhydrocinnamate); 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl) butane; tetrakis [methylene (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)]; thiodiethylene bis-(3,5-di-tert-butyl-4-hydroxy) hydrocinnamate; octadecyl 3,5-di-tert-butyl-4-hydroxyhydrocinnamate; 4,4'-butylidene bis(6-tert-butyl-3 methyl phenol); 0,0-di-n-octadecyl-3,5-di-tert-butyl-4-hydroxybenzyl phosphonate; and N,N'-hexamethylene bis (3,5-di-tert-butyl-4-hydroxyhydrocinnamamide). A preferred phenolic anti-oxidant is

Irganox™ 1076 anti-oxidant, available from Ciba-Geigy Corp.

5 The level of ion content in a polymeric impact
modifier is determined primarily by factors involved in
its preparation. A polymeric impact modifier suitable
for use herein can be prepared by any one of several
polymerization methods including, for example, bulk,
10 solution, precipitation, suspension or emulsion
polymerization. In bulk polymerization, the polymeric
product remains soluble in its own monomer, whereas in
solution polymerization a solvent is added to the
reaction medium which dissolves the monomer and the
polymeric product. In precipitation polymerization, the
15 polymeric product precipitates out of the reaction
medium as it is formed. In suspension polymerization,
polymerization occurs in monomer globules which are
suspended in an aqueous dispersion. In emulsion
polymerization, polymerization occurs in an aqueous
20 system on monomer which has diffused into micelles
formed by surfactants. Acid or base addition to adjust
pH is important in emulsion and suspension methods.

25 In addition to the monomer(s) to be
polymerized, these polymerization methods typically also
involve use in the reaction medium of substances which
function as polymerization facilitators to increase the
favorability of the polymer-formation reaction. For
30 example, free-radical or ionic initiators are frequently
used to start a polymerization reaction, and surfactants
are important in the operation of methods such as
suspension or emulsion polymerization, as mentioned
above. An initiator usually becomes chemically bound as
part of a polymer chain. With a similar effect, a small

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but significant amount of surfactant often physically adheres to the surface of, or becomes confined within, a polymer product, thereby becoming an unintended, residual component of the polymer product when it is recovered in final form. A polymerization initiator may
5 contain an ionic or ionically charged fragment, and an adhered surfactant may contain, or be in the form of, an ion. When an initiator containing an ionic fragment and/or an ionic adhered surfactant is present in the
10 finally produced form of a polymeric impact modifier, the thermal stability of a polycarbonate composition with which the impact modifier is admixed is adversely affected if the ion content of the impact modifier is greater than the limits described herein.

15
The ions present in a polymeric impact modifier promote degradation in the components of the composition at elevated temperatures from chain scission, decomposition and/or transesterification. Polymer
20 degradation which occurs at elevated temperature because of the presence of such ionic species is often manifested by molecular weight loss, discoloration, splay marks from off-gassing and diminished mechanical
25 properties. Because the use of anti-oxidants is not always an adequate means of preventing the harmful effect ionic residues can have on the thermal melt stability of a composition containing a polymeric impact
30 modifier, it is important that the residual amount of a polymerization facilitator in ionic form be reduced in a polymeric impact modifier to a thermal-melt-stabilizing ion amount, but, in any event, to (i) in a polymeric impact modifier containing more than 1.0 up to 5.0 wt percent anti-oxidant, (A) an ion content of sodium and potassium ions of not more than 1,500 ppm and preferably

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not more than 1,000 ppm, and (B) an ion content of all ions of not more than 1,700 ppm; and (ii) in a polymeric impact modifier containing 0.1 to 1.0 wt percent anti-oxidant, (A) an ion content of sodium and potassium ions of not more than 800 ppm and preferably not more than 650 ppm, and (B) an ion content of all ions of not more than 1,500 ppm. The compositions of this invention, containing such low-ion impact modifiers, are therefore characterized as having increased thermal melt stability as compared to compositions containing an impact modifier which is not of the low-ion variety.

Initiators which are useful in the preparation of a polymeric impact modifier are often formed from peroxides such as the following:

diacyl peroxides such as dibenzoyl peroxide, di(2,4-dichlorobenzoyl) peroxide diacetyl peroxide, dilauroyl peroxide, diisobutyryl peroxide; acetyl alkylsulfonyl peroxides; dialkyl peroxydicarbonates such as di-n-propyl peroxydicarbonate; alkyl peroxyesters such as t-butyl perbenzoate, t-butyl peracetate, 2,5-di(benzoylperoxy)-2,5-dimethylhexane, di-t-butyl diperoxyazelaate, t-butyl peroxy-2-ethyl hexanoate, t-amyl peroctate, 2,5-di(2-ethylhexanoylperoxy)-2,5-dimethyl hexane, t-butyl peroxyneodecanoate; OO-t-alkyl O-alkyl monoperoxycarbonates; di(t-alkylperoxy)ketals such as ethyl 3,3-di(t-butylperoxy)butyrate; dialkyl peroxides such as 2,5-di(t-butylperoxy)-2,5-dimethylhex-3-yne; t-alkyl hydroperoxides; and ketone peroxides.

When a peroxide such as one of the above is used together with a reducing agent (transition metal activator) in a redox system, the free radical initiator formed may carry a charge. If so, since the initiator becomes part of the polymer chain, the molecule may have a charged fragment at a chain end which is chemically bound to the chain. This charged fragment often exists in the form of a sulfate, sulfonate or phosphate ion.

Charged free radical initiators which leave a charged fragment at a chain end may also be formed through radiation. UV irradiation of a photoinitiator system may form charged radicals by intermolecular hydrogen abstraction provided a hydrogen donor compound is present. Typical hydrogen donors have an active hydrogen atom positioned alpha to an oxygen, nitrogen or sulfur. Representative compounds which can undergo hydrogen abstraction to form photoinitiators are benzophenone, benzil, 9,10-phenanthraquinone and 9,10-anthraquinone.

Anionic initiators, such as organolithium compounds, can also leave a charged species on a chain end after propagation.

Use of free-radical initiators not formed in a redox system or by photoinitiation, and use of non-ionic initiators are means for reducing the ion content and/or the content of ionically charged species in polymeric impact modifier prepared by polymerization methods wherein such initiators are used.

Cationic and anionic surfactants and soaps, and amphoteric surfactants having both a positive and

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negative charge, are further examples of polymerization facilitators which are frequently used in the type of polymerization reactions in which polymeric impact modifiers are made. For example, surfactants can be used in emulsion polymerization to form the micelles within which polymerization occurs, and surfactants can be used in suspension polymerization as suspending or dispersing agents to prevent coalescence of the monomer globules in the reaction medium. Ionic surfactants used in aqueous systems typically contain a lipophilic portion in the form of a C_{10} - C_{20} chain which may also include, for example, oxygen atoms, a benzene ring, amide or ester groups, or a double bond. The hydrophilic portion of the surfactant is usually then a cation or anion.

Anionic surfactants typically contain as the hydrophile polar groups such as the carboxylate, sulfonate, sulfate or phosphate groups. Typical counterions found associated with anionic surfactants are ammonium, such as NH_4^+ or di- or triethanolammonium or isopropyl ammonium, those formed from the alkali and alkaline-earth metals (periodic table groups IA and IIA) such as lithium, sodium, potassium, magnesium, calcium and barium, those formed from transition metals such as chromium, manganese, iron, cobalt, nickel and copper, and those formed from other metals such as aluminum, zinc or lead. Representative carboxylate anionic surfactants include polyalkoxycarboxylates such as the

polyethoxycarboxylates represented by the formula $R-[-OCH_2CH_2-]_n-CH_2CO_2M$, where R can be tridecyl, cetyl, isostearyl or nonylphenyl and M is a counterion; and

N-acylsarcosinates such as those represented by the formula $R^1\text{CON}(\text{CH}_3)\text{CH}_2\text{CO}_2\text{M}$, where $R^1\text{CO}$ can be cocoyl, lauroyl or oleoyl, and M is a counterion.

- 5 Representative sulfonate anionic surfactants include alkylbenzenesulfonates such as those represented by the formula $R^2\text{C}_6\text{H}_4\text{SO}_3\text{M}$, where R^2 can be dodecyl, tridecyl, $\text{C}_{10}\text{-C}_{13}$ and nonyl, and M is a counterion;
- 10 naphthalenesulfonates such as those represented by the formula $R^3\text{C}_{10}\text{H}_6\text{SO}_3\text{Na}$, where R^3 can be isopropyl, CH_2O , nonyl or butyl;
- 15 dialkyl sulfosuccinates such as those represented by the formula $R^4\text{O}_2\text{CCH}_2\text{CH}(\text{SO}_3\text{Na})\text{CO}_2\text{R}^4$, where R^4 can be amyl, 2-ethylhexyl, octyl, isobutyl or tridecyl.

- 20 Representative sulfate anionic surfactants include alkyl sulfates such as those represented by $R^5\text{OSO}_3\text{M}$, where R^5 can be lauryl, 2-ethylhexyl, 2-decyl, octyl, decyl or tridecyl, and M is a counterion;
- 25 ethoxylated alcohol sulfates such as those represented by the formula $R^6\text{-}[-\text{OCH}_2\text{CH}_2-]_n\text{-OSO}_3\text{M}$, where R^6 can be $\text{C}_{12}\text{-C}_{15}$ linear, lauryl, tridecyl, myristyl, caprylyl or capryl, and M is a counterion;
- 30 ethoxylated alkylphenol sulfates such as those represented by the formula $R^7\text{C}_6\text{H}_4(\text{OC}_2\text{H}_4)_n\text{OSO}_3\text{M}$, where R^7 can be nonyl or octyl or other alkyl, and M is a counterion;

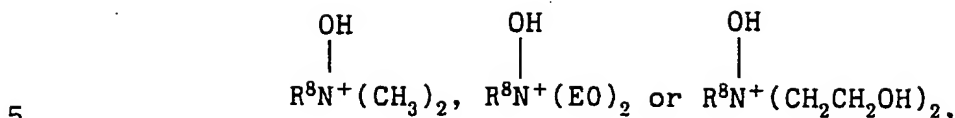
Representative anionic phosphate surfactants include phosphate esters such as butyl, hexyl, 2-ethylhexyl, octyl or decyl phosphate.

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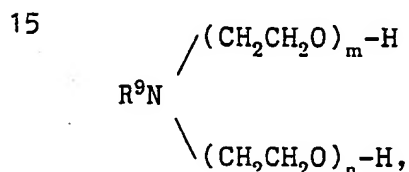
A cationic surfactant carries a positive charge on its hydrophilic portion. This positive charge typically is present in the form of an amino or quaternary nitrogen. Counterions typically found associated with a cationic surfactant are chloride, CH_3SO_4 , sulfate, sulfonate, carbonate or carboxylate ions.

Amine compounds frequently used as cationic surfactants in the preparation of polymeric impact modifiers include, for example, amine oxides, alkyl amine ethoxylates and imidazolines. Representative amine oxides are those described generally by the formula

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10 where R^8 can be cetyl, lauryl, myristyl, stearyl, coco, tallow, hexadecyl, octadecyl, decyl, oleyl, C_{8-15} oxypropyl, and where EO is bis(2-hydroxyethyl). Representative alkyl amine ethoxylates include those described generally by the formula



20 where the amine ($\text{R}^9\text{N}-$) can be derived from coco, soybean, tallow, stearyl, oleyl, rosin or $t\text{-C}_{12-14}$, and $m+n=2-20$.

25 Quaternary ammonium salts useful in processes for preparing polymeric impact modifiers include dialkyldimethyl ammonium salts such as those described generally by the formula $\text{R}^{10}\text{R}^{11}\text{N}(\text{CH}_3)_2\text{A}^-$, where R^{10} and R^{11} can be C_{12-18} , tallow, coco, soya, 30 stearyl, behenyl or erucyl, and A can be Cl or CH_3SO_4 , and

benzalkonium chlorides such as those described generally by the formula $\text{R}^{12}(\text{C}_6\text{H}_5\text{CH}_2)\text{N}(\text{CH}_3)_2\text{Cl}^-$ where R^{12} can be myristyl, oleyl, C_{8-18} , stearyl, cetyl, behenyl, tallow or alkyl.

Use of non-ionic surfactants, use of lower levels of ionic surfactants, and incorporating longer and more numerous wash sections in the polymerization process are means for reducing the ion content in polymeric impact modifier prepared by polymerization methods wherein such surfactants are used.

Additionally, in emulsion polymerization, phase separation of the emulsion polymer product from the aqueous dispersion medium with an organic substance, and use of shear coagulation, freeze coagulation or acid coagulation instead of spray drying for isolation of the emulsion polymer product are also means for reducing residual ion content in the emulsion polymer product.

Hydrophilicity in aqueous systems for non-ionic surfactants is furnished by hydrogen bonding between water molecules and oxygen atoms and hydroxyl, ester and amide groups. Representative non-ionic surfactants which can be used in the preparation of an polymeric impact modifier are as follows:

alcohol ethoxylates described generally by the formula

$R^{13}-(-OCH_2CH_2-)_n-OH$, where R^{13} can be C_6-C_{18} ,

isostearyl, lauryl, cetyl, stearyl, oleyl or tallow and $n=3-30$;

alkylphenol ethoxylates described generally by the

formula $R^{14}C_6H_4-(-OC_2H_4-)_n-OH$, where R^{14} can be nonyl, octyl or dodecyl and $n=1-30$;

carboxylic acid esters;

glycerol esters of fatty acids such as coco, lauric, stearic or oleic acid;

mono- and diesters of polyoxyethylene (polyethylene glycol) and fatty acids such as lauric, pelargonic, oleic or stearic acid;

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sorbitan esters of fatty and tall oil acids such as lauric, oleic, stearic and palmitic acid, or other fatty acid esters of anhydrosorbitol, and polyoxyethylene derivatives thereof;

ethoxylated castor oils;

5 glycol esters of fatty acids; and

carboxylic amides formed from condensation of a

hydroxyalkyl amine such as diethanolamine and a fatty acid such as lauric, linoleic, coco, oleic, myristic, stearic, capric or isostearic acid.

Measurement of the cation content of a polymeric impact modifier, or a polycarbonate composition containing a polymeric impact modifier, is conducted by emission spectroscopy techniques by use of an ashing procedure. For sodium and potassium ions, a flame emission atomic absorption analyzer, for example a Hitachi model 180-70, can be used. For other cations, inductively coupled emission spectroscopy, using for example a Perkin Elmer model 6500 or an ARL model 35000, can be used. Measurement of the anion content of a polymeric impact modifier, or a polycarbonate composition containing an polymeric impact modifier, is conducted by titration.

A variety of additives may be used in the compositions of this invention for protection against thermal, oxidative and ultra-violet degradation. Such additives may be included in the composition at any point during the processing, and the choice as to which additive is employed, if any, is not critical to this invention. Representative of the thermal and oxidative stabilizers which can advantageously be utilized are

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hindered phenols, hydroquinones, phosphites, including substituted members of those groups and/or mixtures of more than one thereof. A preferred phenolic anti-oxidant is Irganox™ 1076 anti-oxidant, available from Ciba-Geigy Corp. Ultra-violet stabilizers such as various substituted resorcinols, salicylates, benzotriazoles, benzophines, hindered amines and hindered phenols can also be usefully included in the compositions of this invention, as can be lubricants, colorants, fillers such as talc, clay or mica, pigments, ignition resistant additives and mold release agents, and reinforcement agents such as fiberglass. Additives and stabilizers such as the foregoing, and many others which have not been mentioned, are known in the art, and the decision as to which, if any, to use is not critical to this invention. However, such additives, if used, typically do not exceed 5 percent by weight of the total composition, except fillers or reinforcing agents, which may constitute up to 40 percent of the composition.

Illustrative Embodiments. To illustrate the practice of this invention, examples of several preferred embodiments are set forth below. It is not intended, however, that these examples (Examples 1-6) should in any manner restrict the scope of this invention. Some of the particularly desirable features of this invention may be seen by contrasting the characteristics of Examples 1-6 with those of controlled formulations (Control A-F) which do not possess the features of, and are not therefore embodiments of, this invention.

The compositions prepared in Controls A-F and Examples 1-6 were made by dry blending the ingredients

thereof and agitating same in a paint shaker for 7 minutes. The dry blended formulations were then melt mixed in a vented 30mm Werner-Pfleiderer co-rotating, twin screw extruder using a 270°C set temperature and 250 rpm. Each extruded composition was passed through a water bath, chopped into granules and collected for molding. Granules were thoroughly dried in a circulated air oven at 115°C for six hours prior to molding. All samples were prepared by injection molding on a 75 ton (6.8 x 10⁴ kg) Arburg molding machine. Molding temperatures for the barrel and mold were set at 280°C and 190°F (88°C), respectively.

Controls A and B do not contain any polymeric impact modifier ("PIM").

Control A is Calibre®300-10 polycarbonate resin ("PC"), which has a 10 melt flow value (measured in accordance with ASTM Designation D 1238-86, Condition 300/1.2), and is available from The Dow Chemical Company.

Control B contains, in an 80/20 parts by weight ratio, PC and Traytuf™ 9506 polyethylene terephthalate ("PET"), which has a 0.95 inherent viscosity (measured in accordance with ASTM Designation D 4603-86). Traytuf™ 9506 polyethylene terephthalate is available from Goodyear Tire and Rubber Co.

Controls C-F each contain a polymeric impact modifier which does not have an ion content as low as that set forth for the polymeric impact modifier used in the compositions of this invention, however Examples 1-6

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each do contain a polymeric impact modifier which meets the ion content criteria prescribed herein.

- 5 Control C contains, in a 95/5 parts by weight ratio, PC and Paraloid™ 3691 PIM, which is a commercial methyl methacrylate/butadiene/styrene copolymer available from Rohm & Haas Chemical Co., a polymeric impact modifier which does not contain greater than 1.0 wt percent anti-oxidant.
- 10 Control D contains, in a 73/20/7 parts by weight ratio, PC, PET and Paraloid™ 3607 PIM, which is a commercial methyl methacrylate/butadiene/styrene copolymer available from Rohm & Haas Chemical Co., a polymeric impact modifier which does contain greater than 1.0 wt percent anti-oxidant.
- 15 Control E contains, in a 73/20/7 parts by weight ratio, PC, PET and Paraloid™ 3691 PIM.
- 20 Control F contains, in a 73/20/7 parts by weight ratio, PC, PET and KaneAce™ B-56 PIM, which is a commercial methyl methacrylate/butadiene/styrene copolymer available from Konica Texas, a polymeric impact modifier which does not contain greater than 1.0 wt percent anti-oxidant.
- 25 Example 1 contains, in a 73/20/7 parts by weight ratio, PC, PET and P-3607A PIM, which is an experimental methyl methacrylate/butadiene/styrene copolymer prepared by Rohm & Haas Chemical Co. for The Dow Chemical Company, a polymeric impact
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modifier which does contain greater than 1.0 wt percent anti-oxidant.

Example 2 contains, in a 73/20/7 parts by weight ratio, PC, PET and P-3607B PIM, which is an experimental methyl

5 methacrylate/butadiene/styrene copolymer prepared by Rohm & Haas Chemical Co. for The Dow Chemical Company, a polymeric impact modifier which does contain greater than 1.0 wt percent anti-oxidant.

10 Example 3 contains, in a 73/20/7 parts by weight ratio, PC, PET and P-8967 PIM, which is an experimental methyl

15 methacrylate/butadiene/styrene copolymer prepared by Rohm & Haas Chemical Co. for The Dow Chemical Company, a polymeric impact modifier which does contain greater than 1.0 wt percent anti-oxidant.

20 Example 4 contains, in a 73/20/7 parts by weight ratio, PC, PET and PA-2130 PIM, which is an experimental methyl

25 methacrylate/butadiene/styrene copolymer prepared by M&T Chemical Co. for The Dow Chemical Company, a polymeric impact modifier which does contain greater than 1.0 wt percent anti-oxidant.

Example 5 contains, in a 73/20/7 parts by weight ratio, PC, PET and PA-2279 PIM, which is an experimental methyl

30 methacrylate/butadiene/styrene copolymer prepared by M&T Chemical Co. for The Dow Chemical Company, a polymeric impact modifier which does contain greater than 1.0 wt percent anti-oxidant.

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Example 6 contains, in a 73/20/7 parts by weight ratio, PC, PET and Paraloid™ 3339 PIM, which is a commercial butyl acrylate elastomer available from Rohm & Haas Chemical Co., a polymeric impact modifier which does not contain greater than 1.0 wt percent anti-oxidant, acrylates being inherently more stable than dienes because of lower levels of residual unsaturation, resulting in latices of larger particle size.

Samples of the various polymeric impact modifiers contained in the compositions of Controls C-F and Examples 1-6 were subjected to emission spectroscopy to determine the content of sodium, potassium and calcium ions therein. For sodium and potassium ions, a flame emission atomic absorption analyzer, Hitachi model 180-70, was used. For calcium, inductively coupled emission spectroscopy, using a Perkin Elmer model 6500, was performed. The results of those tests performed on the various polymeric impact modifiers ("PIM") are shown in Table II, wherein ion content is stated in ppm.

Table II
 Na^+ , K^+ and Ca^{2+} Content of
 Polymeric Impact Modifiers

PIM	Control or Example	Anti-oxidant at greater than 1 wt%	Na^+	K^+	Ca^{2+}	Total Na^+ , K^+ and Ca^{2+} ions
Paraloid™ 3607	D	Yes	1,800	6	4	1,810
Paraloid™ 3691	C and E	No	1,600	520	8	2,128
Kaneace™ B-56	F	No	870	159	22	1,051
P-3607A	1	Yes	470	400	73	943
P-3607B	2	Yes	53	82	2	137
P-8967	3	Yes	560	390	113	1,063
PA-2130	4	Yes	160	80	2	242
PA-2279	5	Yes	16	28	1,600	1,644
Paraloid™ 3339	6	No	640	5	690	1,335

5 The data in Table II show that Paraloid 3607™
PIM, a modifier which does contain greater than 1 wt
percent anti-oxidant, contains more than 1,500 sodium
and potassium ions, and Paraloid 3691™ PIM and Kaneace
B-56™ PIM, modifiers which do not contain greater than
1 wt percent anti-oxidant, contain more than 800 sodium
and potassium ions. Each of the modifiers used in
10 Examples 1-6 does, however, have an ion content within
the levels set forth above for this invention.

15 Samples of the compositions of Controls A-F and
Examples 1-6 were subjected to thermogravimetric
analysis on a DuPont Instruments 951 Thermogravimetric
Analyzer connected to a DuPont Instruments
Thermalanalyst 2100 to determine the percent weight loss
of each sample when it had been held at a constant
temperature (in this case 310°C) in air for periods of
20 ten, twenty and thirty minutes. The results of that
test are reported in Table III.

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Table III
Weight Loss Results for Controls A-F and Examples 1-6

	Controls						Examples					
	no PIM		with PIM				1	2	3	4	5	6
	A	B	C	D	E	F						
Anti-oxidant present in PIM at more than 1.0 wt%			No	Yes	No	No	Yes	Yes	Yes	Yes	Yes	No
Total Na ⁺ and K ⁺ content of PIM	0	0	2,120	1,806	2,120	1,029	870	135	950	240	44	645
Total Na ⁺ , K ⁺ and Ca ²⁺ content of PIM	0	0	2,128	1,810	2,128	1,051	943	137	1,063	242	1,644	1,335
percent weight loss, 10 minutes	0	0.2	0.2	2.1	5.0	4.8	0.6	0.6	0.8	0.8	0.6	0.8
percent weight loss, 20 minutes	0.008	0.3	0.6	4.0	7.5	7.4	0.9	0.9	1.3	1.3	1.2	1.4
percent weight loss, 30 minutes	0.04	0.6	1.0	5.5	9.8	9.3	1.2	1.3	1.7	1.7	1.7	2.0

The results of the tests performed on Controls A-F and Examples 1-6 show that, among the compositions containing a polymeric impact modifier (Controls C-F and Examples 1-6), those containing a polymeric impact modifier meeting the ion content criteria of this invention have by far a lower percent weight loss, after having been subjected to an extreme temperature for an extended period of time, than the controlled compositions. For example, Control D, which contains a total of 1,806 Na⁺ and K⁺ ions and more than 1.0 wt percent anti-oxidant, experiences a weight loss of 5.5 percent after 30 minutes of heating whereas Example 2, which contains a total of 135 Na⁺ and K⁺ ions, undergoes a weight loss of only 1.3 percent. Similarly, Control E, which contains a total of 2,120 Na⁺ and K⁺ ions and 1.0 wt percent or less of anti-oxidant, experiences a weight loss of 9.8 percent after 30 minutes of heating whereas Example 6, which contains a total of 645 Na⁺ and K⁺ ions, undergoes a weight loss of only 2.0 percent. Similarly desirable low weight loss is also obtained for Examples 1 and 3-5. Controls A and B, which contain no polymeric impact modifier, and Control C, which contains modifier at a very low level, experience low weight loss because the quantity of ions imparted to a composition by the modifier increases as the amount of modifier present in the composition increases.

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These data demonstrate that the thermal melt stability of a composition containing polycarbonate, optionally polyester, and a polymeric impact modifier is substantially improved when the ion content (i) in a polymeric impact modifier containing more than 1.0 up to

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5.0 wt percent anti-oxidant, (A) is an ion content of sodium and potassium ions of not more than 1,500 ppm and preferably not more than 1,000 ppm, and (B) is an ion content of all ions of not more than 1,700 ppm; and (ii) in a polymeric impact modifier containing 0.1 to 1.0 wt percent anti-oxidant, (A) is an ion content of sodium and potassium ions of not more than 800 ppm and preferably not more than 650 ppm, and (B) is an ion content of all ions of not more than 1,500 ppm, as opposed to such compositions containing a polymeric impact modifier not having such low ion content.

Samples of the compositions of Controls B and D-F and Examples 1-6 were also dissolved in methylene chloride, and the polyester and the polymeric impact modifier were removed from the solution leaving only the polycarbonate. The remaining polycarbonate samples were then analyzed on a Hewlett-Packard 1090 liquid chromatograph using a gel permeation column to determine the weight-average molecular weight ("Mw"), the number-average molecular weight ("Mn"), and polydispersity (Mw/Mn, "Disp.") of each sample. The analytical test was performed on samples of each composition which have been melt mixed in an extruder ("Pellet"), and on samples which have been held at 300°C for seven minutes in a melt flow analyzer, or in any similar apparatus with an enclosed heating chamber ("Strand"). The results of those tests are reported below in Table IV.

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Table IV, Molecular Weights

	Pellet			Strand		
	Mw	Mn	Disp.	Mw	Mn	Disp.
Control B	29,906	10,993	2.73	27,762	9,915	2.80
Control D	31,037	10,446	2.84	30,334	8,458	3.59
Control E	30,536	11,000	2.78	25,650	9,952	2.58
Control F	27,390	10,251	2.67	24,080	9,485	2.54
Example 1	30,741	10,978	2.80	27,893	8,758	3.18
Example 2	29,835	10,696	2.79	28,338	9,087	3.12
Example 3	29,985	10,565	2.84	27,360	8,198	3.34
Example 4	29,412	10,837	2.71	26,607	8,283	3.21
Example 5	27,725	10,393	2.67	26,435	8,311	3.18
Example 6	31,219	11,331	2.76			2.96

5 The data in Table IV show that the polydispersity of a polycarbonate present in a composition of this invention, which contains a low ion polymeric impact modifier, is higher after 300°C heat aging than that of a polycarbonate compounded with a modifier which does not meet the ion content criteria of this invention.

10 It is within the skill in the art to practice this invention in numerous modifications and variations in light of the above teachings. It is, therefore, to be understood that the various embodiments of this invention described herein may be altered without
15 departing from the spirit and scope of this invention as defined by the appended claims.

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1. A composition of matter comprising, in admixture, an aromatic polycarbonate, and a polymeric impact modifier which (a) contains 5-80 wt percent rubber, (b) contains more than 1.0 wt percent up to 5.0 wt percent anti-oxidant, and (c) has a content of sodium ions and potassium ions of not more than 1,500 weight parts per million.

2. The composition of Claim 1 wherein the polymeric impact modifier has a content of sodium ions and potassium ions of not more than 1,000 weight parts per million.

3. The composition of Claim 1 wherein the polymeric impact modifier has a content of all ions of not more than 1,700 weight parts per million.

4. The composition of Claim 1 wherein the composition has a content of either cations or anions of not more than 1,200 weight parts per million.

5. The composition of Claim 1, 3 or 4 further comprising an aromatic polyester.

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6. A composition of matter comprising, in admixture, an aromatic polycarbonate, and a polymeric impact modifier which (a) contains 5-80 wt percent rubber, (b) contains 0.1 to 1.0 wt percent anti-oxidant, and (c) has a content of sodium ions and potassium ions of not more than 800 weight parts per million.

7. The composition of Claim 6 wherein the polymeric impact modifier has a content of sodium ions and potassium ions of not more than 650 weight parts per million.

8. The composition of Claim 6 wherein the polymeric impact modifier has a content of all ions of not more than 1,500 weight parts per million.

9. The composition of Claim 6 wherein the composition has a content of either cations or anions of not more than 1,200 weight parts per million.

10. The composition of Claim 6, 8 or 9 further comprising an aromatic polyester.

11. A composition of matter comprising, in admixture, an aromatic polycarbonate and a polymeric impact modifier containing 5-80 wt percent rubber, said composition having an ion content of not more 1,200 weight parts per million of either cations or anions.

12. The composition of Claim 11 further comprising an aromatic polyester.

13. A composition of matter comprising, in admixture, an aromatic polycarbonate, an aromatic

polyester and a polymeric impact modifier containing 5-80 wt percent rubber, said composition being characterized in that it experiences no more than 2.0 percent weight loss after heating at 310°C in a thermogravimetric analyzer for ten minutes.

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14. A composition of matter comprising, in admixture, an aromatic polycarbonate, an aromatic polyester and a polymeric impact modifier containing 5-80 wt percent rubber, said composition being
10 characterized in that it experiences no more than 3.5 percent weight loss after heating at 310°C in a thermogravimetric analyzer for twenty minutes.

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15. A composition of matter comprising, in admixture, an aromatic polycarbonate, an aromatic polyester and a polymeric impact modifier containing 5-80 wt percent rubber, said composition being
characterized in that it experiences no more than 5.0
20 percent weight loss after heating at 310°C in a thermogravimetric analyzer for thirty minutes.

16. The composition of Claim 13, 14 or 15 wherein the polymeric impact modifier contains more than
25 1.0 wt percent up to 5.0 wt percent anti-oxidant, and has a content of sodium ions and potassium ions of not more than 1,500 weight parts per million.

17. The composition of Claim 16 wherein the
30 polymeric impact modifier has a content of all ions of not more than 1,700 weight parts per million.

18. The composition of Claim 13, 14 or 15 wherein the polymeric impact modifier contains 0.1 to

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1.0 wt percent anti-oxidant, and has a content of sodium ions and potassium ions of not more than 800 weight parts per million.

5 19. The composition of Claim 18 wherein the polymeric impact modifier has a content of all ions of not more than 1,500 weight parts per million.

10 20. A composition of matter comprising, in admixture, an aromatic polycarbonate, an aromatic polyester and a polymeric impact modifier, said composition having a polydispersity (ratio of weight average molecular weight to number average molecular weight) between 2.85 and 3.5, as determined by gel permeation chromatography after the composition has been
15 held for seven minutes at 300°C in an apparatus with an enclosed heating chamber.

20 21. A method of improving the thermal melt stability of an impact modified aromatic polycarbonate composition, comprising
(a) providing (i) a polymeric impact modifier which contains more than 1.0 wt percent up to 5.0 wt percent anti-oxidant, and has a content of
25 sodium ions and potassium ions of not more than 1,500 weight parts per million; or (ii) a polymeric impact modifier which contains 0.1 to 1.0 wt percent anti-oxidant, and has a content
30 of sodium ions and potassium ions of not more than 800 weight parts per million; and
(b) blending one of said polymeric impact modifier with an aromatic polycarbonate.

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22. The method of Claim 21 wherein step (b) further comprises blending one or both of said polymeric impact modifiers with an aromatic polycarbonate and an aromatic polyester.

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INTERNATIONAL SEARCH REPORT

PCT/US 91/03468

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08L69/00 ; C08L67/00 ; C08L101/00

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System

Classification Symbols

Int.Cl. 5

C08L ; C08F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,23 291 (BAYER AG) February 4, 1981 see page 14, line 21 - line 28; claims 1-3 ---	1,6,21
A	GB,A,2 193 966 (NIPPON GOHSEI KAGAKU KOGYO KABUSHIKI KAISHA) February 24, 1988 see page 1, line 26 - line 32; claims 1-6 ---	1
A	FR,A,2 369 320 (SUMITOMO CHEMICAL COMPANY LTD) May 26, 1978 see claims 1-5 ---	1
A	W.F. CHRISTOPHER AND D.W. FOX 'POLYCARBONATES' 1962 , REINHOLD PUBLISHING CORPORATION , NEW YORK see page 29, line 10 - line 13 see page 89, line 10 - line 21 ---	1

¹⁰ Special categories of cited documents : ¹⁰¹¹ "A" document defining the general state of the art which is not considered to be of particular relevance¹² "E" earlier document but published on or after the international filing date¹³ "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)¹⁴ "O" document referring to an oral disclosure, use, exhibition or other means¹⁵ "P" document published prior to the international filing date but later than the priority date claimed¹⁶ "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention¹⁷ "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step¹⁸ "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.¹⁹ "A" document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

18 OCTOBER 1991

Date of Mailing of this International Search Report

24 OCT 1991

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

DECOCKER L.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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A	WO,A,8 705 920 (GENERAL ELECTRIC COMPANY) October 8, 1987 see claims 1-9 ---	1,5,6, 10, 13-15, 20,21
A	EP,A,115 885 (STAMICARBON B.V.) August 15, 1984 see claims 1-9 ---	1,6,21

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9103468
SA 49311

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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18/10/91

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